CHAPTER 3
EVALUATING EMISSIONS FACTORS, MODELS & INVENTORIES WITH PAMS DATA

3.1 INTRODUCTION

One of the principal benefits of the PAMS monitoring network is the feedback it provides to the various elements of the ozone regulatory program. Emissions inventories are an important element of the ozone program. PAMS provides valuable feedback which can be used to evaluate and improve the inventory. This chapter begins with a brief background description of emissions inventories and potential inventory problems that PAMS data can elucidate.   This introduction is followed by examples illustrating the use of PAMS data to evaluate and refine emissions inventories. These examples are separated into two sections: direct comparisons of the inventory components with measured data and more refined analyses using multivariate and chemical mass balance analyses. The chapter concludes with a more detailed description of the analytical techniques.

3.2 BACKGROUND

Emissions inventories have long been a cornerstone of air quality management. Emissions estimates are important for determining applicability of sources in permitting and control programs, ascertaining the air quality impact of sources and appropriate mitigation strategies, and a number of other related applications by an array of users, including federal, state, and local agencies, consultants, and industry. Data from source-specific emissions tests or continuous emissions monitors are usually preferred for estimating a source's emissions because those data provide the best representation of the tested source's emissions. However, test data from individual sources are not always available and, even if they are, the tests only represent a snapshot in time and may not reflect the variability of actual emissions over time. Continuous emissions monitors could resolve this variability concern but are expensive and technologies are unproven for some pollutants. Thus, emissions factors are frequently the best or only method available for deriving emissions estimates, in spite of their limitations.

Emissions estimates are the product of emissions factors established for various source categories of VOC, NO_x and CO as well as activity levels established for each source category. Emissions factors describe the amount of emissions produced per unit of activity at a source. Examples are "lbs. NO_x produced per megawatt of power produced by a utility" or "grams of VOC produced per vehicle mile traveled by the current mix of automotive sources". Emissions factors are often based on measurements made for a limited number of sources within a broad

source category. Further, the measurements may be dated or made at geographical locations far removed from the area of interest.

The activity level estimate from a source describes the number of units produced by a source, which result in the by-product of pollutant emissions. In the two examples cited above, activity levels would be the megawatts of power produced by the utility in question and the vehicle miles traveled by the automotive fleet over a period of interest. In some cases, such as for utilities, activity levels can be determined with considerable reliability. In others however, activity levels must be estimated using surrogate indicators like population, sales figures and employment statistics.

Emissions inventories are used for a variety of purposes. Some of these, like use in a photochemical modeling exercise, require a high degree of spatial and temporal resolution, as well as information about the chemical composition of the emissions. Emissions models are used to develop this information which, in turn, is used as input to the photochemical models. Emissions models need to address issues like, "how are emissions distributed within a city?", and "what kind of temporal or diurnal patterns are reasonable to assume for the emissions from various source categories?" These estimates are obtained from emissions factors, estimated activity levels, estimated spatial/temporal patterns of activity using various surrogates, available information on sensitivity of emissions factors to meteorological conditions and limited information on the chemical composition of emissions from the various source categories.

The concept of using ambient measurements to improve emissions models, factors and inventories is not new. In 1985, Air Pollution Control Association Specialty Conference on Receptor Methods for Source Apportionment, several authors discussed the potential application of receptor models to identify unknown sources or source categories. In that conference, several authors demonstrated the use of receptor models to interpret speciated ambient measurements of particulate matter, (Pace, 1986). One very early investigation to reconcile atmospheric hydrocarbons with sources was conducted in 1974, (Mayrsohn). Recently, a critical evaluation of studies that used ambient data to infer weaknesses in ozone precursor emissions inventories was completed, (Yarwood).

Identifying possible discrepancies in the inventory compared to the ambient data is only the first step in the process. This has to be followed up with detailed emissions surveys for sources around the monitor, careful review of the speciation and temporal profiles used to convert the inventory to something compatible with the monitored results. This is costly and time-consuming, but is the only way to truly improve the quality of an emissions inventory. Therefore, while PAMS data can provide a very good tool for assisting in the overall improvement of emissions inventories, it does have certain limitations as discussed above. This Chapter is not designed a "cookbook" on how to use PAMS data; rather, its intent is to illustrate some of the

effective uses of PAMS data for inventory evaluation.

3.2.1 Potential Inventory Problems

Potential problems that can be identified (and potentially resolved) through the use of PAMS data are of two general types: emissions factor/model representativeness and proper application of the factors, including spatial/temporal resolution. These issues are summarized in Table 3-1.

3.2.2 Difficulties in Comparing Ambient Data and Emissions Estimates

The use of ambient measurements to corroborate emissions estimates are potentially useful for focusing attention on particular assumptions underlying the emissions inventory. There are many limitations associated with using ambient data to evaluate emissions inventories and care should be taken to not over-simplify the results of such comparisons. A discussion of some of the difficulties and issues follows:

Spatial Representativeness
One issue that has not been completely resolved is determining which emissions area to compare with the ambient measurement. Several gridding techniques have been proposed [Pace (1978) and Main]. These basically consist of developing finely gridded micro inventories for comparison with the ambient data, forming concentric cells or grids representing increasingly an larger area around the site. Figure 3-1 represents one such gridding system used to analyze Hartford emissions data (Main). Under transport conditions, it may be necessary to use emissions from a sector upwind of the monitor for the time just preceding the sample collection. The representativeness of the monitoring network also needs be considered. To fully evaluate an inventory, several monitoring sites may be needed depending on the complexity of the sources and the nature of the area. The mix of emissions sources, the meteorology and the location of the monitor all influence the analysis. a consistent (or inconsistent) analysis at one urban monitor may not mean that the emissions estimates in all parts of the area are good (or poor). To get a sense of the representativeness of the PAMS data for inventory evaluation, it is useful to perform correlation analyses of total VOC and VOC species to see how they compare with data from other sites.

Meteorological Issues
The most important influence to consider when comparing emissions estimates with ambient data is to account for the influence of meteorology. All non-point source emissions in an inventory are considered to occur at the surface and may be appropriate to evaluate with ambient data. However, elevated point sources may not be accurately represented at an emissions-oriented monitor near the ground due to meteorological influences. Also, the relationship

between emissions rates and ambient air concentrations is quite complex, depending on many meteorological parameters such as wind speed and direction, atmospheric stability, temperature inversion heights, and horizontal and vertical diffusion rates. Therefore, careful analysis of the meteorological data at the site needs to accompany the analysis of the ambient data in order to define the appropriate comparisons to make.

Chemical Reactivity

As stated previously, emissions inventories are based on emissions factors and activity level estimates. These emissions factors are available for the criteria pollutants (NO_x, VOC, CO, PM, SO_2). In reality, VOC emissions are a composite of multiple hydrocarbon compounds generated through some type of chemical process. These compounds react and form other compounds once they are released into the atmosphere. Some of these reactions occur very rapidly and others may take hours to occur. This is important to consider because a monitor is measuring a point in time and may not reflect the original mix of emitted species that is being transported into that area at that point in time due in part to these chemical reactions. Thus, along with the meteorological influences mentioned above, the reactivity of the emissions from sources near the monitor may lead to concentrations or ratios that are inconsistent with the original profile of the area's emitted species.

3.3 PAMS RESULTS

PAMS data have already been useful in analyses to evaluate the viability of the emissions inventory. However, the full potential of these data are just beginning to be realized. A recent report (Yarwood et al., 1994) evaluated 25 studies related to this topic and provided objective and critical overview of each. Appendix A tabulates some of the key analyses identified in that report. When researchers have access to the vast body of data being collected in PAMS, the full benefit of the PAMS network for evaluating emissions data can be realized.

PAMS data can be useful to the regulatory community in three ways. First, measured concentrations of certain indicator species can be compared with emissions estimates. $NMOC/NO_x$ ratios, and comparisons of inventory estimates of key VOC species with ambient measurement of these species are two common types. Second, quantitative analyses, such as Chemical Mass Balance (CMB) can be used to compare emissions estimates for specific source categories. CMB is a sophisticated least squares statistical method for identifying the most likely source categories contributing to a given ambient sample, based on the relative amounts of each species present in the sample and the relative amounts of those same species present in the emissions of source categories. The CMB differs from tracer methods in that the indicator species need not be unique to a given source category. Third, PAMS data provide an opportunity to compare the PAQSM-estimated species concentrations with ambient measurements of these species at the time of day that the measurements were taken. The value of such comparison is

obvious, both for inventory evaluation and to verify the transformation algorithms in the model. Unfortunately, chemical mechanisms commonly used in photochemical models aggregate emissions species. Thus, our ability to compare predicted and observed precursor species is limited.

This section begins with a discussion of key tracer species that can be indicative of source presence and strength at the PAMS site. Then it presents examples of both qualitative and quantitative methods that can yield valuable information about the inventory. Since the PAMS network is relatively new, this section will supplement PAMS-based examples with examples from other databases that have similar data to that being collected by PAMS.

3.3.1 Examples of Indicator Species or Compounds (Tracers)

If a chemical species measured in PAMS is unique to a particular source, considerable information can be gleaned without employing sophisticated receptor modeling techniques. e.g., CMB. These chemical species, unique or nearly unique to one source or source type, are referred to as "indicator species, compounds or tracers of convenience".[1] Table 3-2 identifies some PAMS target compounds frequently used as tracers. The Chemical Mass Balance model (see Section 3.5 for examples) is a more powerful technique because it is not limited to tracers that are uniquely associated with only one source type.

Discussion of Specific Tracers
As noted in Table 3-2, various compounds are useful in evaluating the emissions of industrial manufacturing sources. Usually, the presence of these compounds may be determined by discussion with the emissions inventory specialist. Benzene, propene, toluene, and ethene have also been suggested as tracers for motor vehicle exhaust. Benzene was used extensively in various solvent intensive industrial processes until toxicity concerns and subsequent regulations greatly curtailed that type of usage. Benzene still falls short of being an ideal tracer for motor vehicle exhaust since it is also present in evaporative emissions and emissions from various combustion processes. The introduction of reformulated gasoline (RFG) in select urban areas in 1995 (as mandated by the Clean Air Act Amendments of 1990) will impact the chemical makeup of motor vehicle exhaust. RFG exhaust and evaporative emissions speciation profiles have already been developed and included in the 1993 SPECIATE database update, though future

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[1] Since very few emissions sources have their own distinct tracer, the scope of tracer of analysis is limited. a few methods for overcoming this handicap have been explored, including adjusting the tracer concentrations to account for other sources (Yarwood 1994). Another alternative utilized (to some limited degrees of success) is the intentional release of an "artificial" tracer into source emissions. Concentrations of this distinct artificial tracer found at a receptor, indicate a definite non-zero contribution of emissions from the source. This option has been limited to point sources since it would be impractical to inject tracer material at area sources. Even with point sources, though, large costly amounts of the tracer material are required to produce detectable concentrations at the receptor (Yarwood 1994).

refinement of the profiles is anticipated[2].   Carbon monoxide (CO), a criteria pollutant, is perhaps the best of all motor vehicle exhaust tracers and should be used to supplement other tracer information for mobile sources when available.

Butane has been noted as an excellent tracer for gasoline evaporative emissions. Butane accounts for approximately 35% of those type emissions. Isopentane, one of the largest NMOC components, is also regarded as a tracer for gasoline vapor. Almost all evaporative emissions are ascribed to vehicle-related sources (U.S.EPA, 1991a).

Isoprene, α-pinene and β-pinene are the only PAMS compounds predominantly associated with natural emissions and thus are the only available for use as tracers.   All, however, are extremely reactive. Because all three compounds are very reactive, analysis relating ambient concentrations to source emissions often result in emissions underestimations. Unfortunately, there are no biogenic tracer alternatives.

Toluene has been mentioned as a tracer for motor vehicle exhaust. It, like other exhaust components, is generally present in characteristic ratios. Excess beyond this characteristic portion, can be used as a tracer of graphic arts and surface coating processes. Both of these types of operations commonly use solvent-based paints or inks. Propane can be used as an area-source indicator (liquefied petroleum gas use) or a point-source indicator (oil/gas production and petroleum refineries). Moderate to high concentrations of ethane can indicate natural gas use or leakage but, as noted before, measurement difficulties are commonly encountered. Isobutane has been suggested as a tracer for consumer product emissions; most aerosol products now utilize isobutane as a propellant since chlorofluorocarbons were banned (Stoeckenius et al.).

Indicator species afford data analysts an opportunity to characterize source types from ambient concentrations with minimum inputs. Although many PAMS target species are emitted from multiple sources, some are typical to only one or two, like those in Table 3-2.   When using tracers to ascertain relative source emissions, one must be careful to consider the ramifications of reactivity. Reactions breaking down tracer compounds can result in incorrect estimations of the source's impact.   Interpretation of tracer data is straightforward if the compounds are unique and inert. As mentioned above, complex software models such as CMB can be used if the tracer is not unique or if multiple tracers are available for several sources.

Using Tracer Data

To be an effective tracer, a compound should be relatively inert. Otherwise, photochemical reactions breaking the compound down will result in altered (usually reduced, but possibly increased) ambient concentrations of the compound thus precipitating a mis-estimation of

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[2] U.S. EPA. "SPECIATE database." URL: http://134.67.104.12/html/chief/spec-dn.htm. October 29,1996.

the source emissions impact. Unfortunately, many PAMS target compounds are extremely reactive. Thus, one option to utilize these reactive species as tracers is to use ambient concentrations from hours when emissions are generally high and photochemical reactivity is relatively low. The 6-9 a.m. time frame is frequently mentioned for mobile related analysis. A second option is to consider only tracers which are relatively unreactive (i.e., lifetime greater than eight hours).

Ambient air samples containing inert tracers can be used to estimate the concentration contribution of all emissions (or an emission category total such as TNMOC) from the tracer source. To compute the contribution of the total emissions P from source j, simply divide the observed concentration of the tracer t by R, the relative proportion of the tracer component found in the emissions at the source: $P_j = t_j / R_j$. To find the concentration associated with a specific pollutant (p), substitute r, the relative proportion of the tracer to the specific pollutant (at the source) for R thus giving: $p_j = t_j / r_j$. If the indicator species is not truly unique, the preceding formulas can be used to compute upper limits of the emissions impact. Likewise, if a tracer is somewhat reactive, the formulae can give a lower limit to the emissions impact.

For example, a local gasoline emissions profile shows that butane accounts for 35% (weight percent) of total non-methane hydrocarbon emissions (NMHC). An ambient monitor recorded average butane levels of 3 μg/m^3 (converted from ppbC). Hence, $R = .35$ and $t = 3$. We can therefore estimate the total NMHC associated with gasoline evaporative emissions (P) to be about 8.6 μg/m3 ($P = 3 / .35$). Since butane is also present in vehicle exhaust emissions, the computed figure should be considered an upper bound. If the gas profile also showed that cyclopentane (another PAMS target compound) accounted for .5 weight percent of NMHC, we know that the relative proportion of the butane tracer to it (r) is 7 (35 / .5) and we can apportion .4 μg/m^3 of cyclopentane to that particular source ($p= 3 / 7$). The computed μg/m^3 values can be converted to ppbC using species-specific conversion factors.

3.3.2 Examples Using NMOC/NO$_x$, Directional and Time Series Analyses.

Ratio information is often of great use for making qualitative judgments about whether a source category or individual source is missing from the inventory, misplaced or otherwise grossly mischaracterized. The use of ratios or single species which serve as tracer compounds for a source category is enhanced when combined with several of the other screening tools described in this Section. This Section also describes time series analyses and the use of wind direction information to evaluate the direction associated with high concentrations of speciated data.

NMOC/NO$_x$ Ratios and Ratios of Other Species

As mentioned previously, problems associated with species reactivity must be addressed before the ratio approach can be used effectively. One way is to confine the analysis to periods of

the day in which atmospheric chemistry is minimal. This is generally at nighttime or shortly after sunrise (e.g., 6-9 am). During such periods, one must take care to account for the lack of vertical mixing in the atmosphere (e.g., by excluding all elevated sources from the inventory) when comparing emission-derived and measured ambient ratios for a diverse set of sources since the surface level monitoring site is unlikely to see any contribution from these sources at this time of day. In general, excluding elevated point sources in calculating the emissions-derived $NMOC/NO_x$ ratio increases the calculated ratio because elevated point sources are far more prevalent for NO_x emissions than for VOC. The second approach for discounting effects of reactivity is to consider only ratios of pollutants which are relatively unreactive [see Altshuller, Lewis or Carter for further information on reactivity].

Use of ratio data as a possible means for corroborating inventory estimates is illustrated in Figures 3-2 and 3-3. Figure 3-2 plots 6-9 am $NMOC/NO_x$ ratios measured at two suburban New Jersey sites during summer 1993 (NESCAUM). After excluding certain sources from consideration (as described above) the emission-derived ratio can be compared to the range of observed ratios to check for possible gross errors in the estimates. If a plot like Figure 3-2 is comprised of data from more than one site, the data can be scrutinized to see whether there are any apparent systematic differences in the ratios observed at different sites. For example, in Figure 3-2, ratios at the Plainfield site appear to be somewhat higher than those measured at Newark. This interpretation can be compared with the emission-derived estimates. If not similar, other analyses such as looking at the ratio of a reactive to less reactive species could be explored to see whether the difference in the measured $NMOC/NO_x$ ratios is attributable to greater transport at one of the sites or some alternative explanation. If the findings are not consistent with alternate explanations, this may imply a potential problem with the inventory near one or both of the sites.

Figure 3-3 illustrates how observed ratios among species might be used as a means of identifying presence of emissions from certain source categories (Chameides et al.). For example, in the figure there is a high correlation observed between trans-2-pentene and cis-2-butene. This implies a common source for the two species is impacting the monitoring site. One can check the inventory of nearby sources to see whether the emissions estimates are consistent with these observations.

Directional Associations
As the name implies, this screening analysis entails subdividing air quality observations into bins which correspond with different measured wind directions. Often eight principal wind directions are considered. Distributions of various air quality indicators can then be constructed for each of the wind directions. Comparing differences in the air quality distributions among wind directions can be readily done by graphically displaying the data in a "pollution rose". Figure 3-4 illustrates the procedure using ozone as the air quality indicator (Incecik et al., 1995). The

procedure is amenable to using a variety of air quality indicators, including individual VOC species or ratios of species.

Use of directional associations between pollutant species or ratios enables those reviewing the inventory to better focus on portions of the inventory which may need further verification and refinement. For example, for a given wind direction one can compare observed distributions of species or ratios of species with emissions estimates which are upwind from the monitoring site. Presence or dominance of species which appear to be unaccounted for by the upwind emissions estimates will help direct the analyst's attention to geographical locations where the inventory may need improvements. In a similar vein, presence of pollutant ratios which seem inconsistent with proportions of species in upwind emissions estimates would also help direct a review of the assumptions, methodology and data base underlying the emissions estimates.

Time Series Analyses

Time series analyses of VOC, its species, NO, NO_2, NO_x and ratios of VOC to NO_x are potentially useful for corroborating whether assumptions in emissions models about diurnal emissions patterns are supportable. In addition, time series plots can serve as useful guides in helping the analyst decide which portion of the inventory to compare with ambient concentrations at different times of day. For example, if a time series plot indicated that a source category impacted a monitor at midday, but not at 6-9 am, this would serve as additional rationale for excluding that source from the inventory in the 6-9 am comparison. Third, time series analyses can, when used with other information (described later), help the analyst corroborate whether assumptions in the emissions model about sensitivity of emissions to meteorological conditions are consistent with observations.

Figure 3-5 shows PAMS-based time series plots on weekdays and weekends for three VOC species (Stoekenius et al.). Recall that acetylene is a tracer for automotive exhaust. One can see from comparing weekday vs. weekend time series for acetylene that the two time series differ. This is consistent with a possible need to use differing diurnal activity levels for automotive sources on weekends vs. weekdays. Figure 3-6 is a time series plot of isoprene data measured at a suburban site in Houston (Stoekenius et al.). Note the distinctly different diurnal pattern for isoprene vs. the ones for other species shown in Figures 3-5 and 3-6. The observed pattern is consistent with our understanding of how the emissions factor for isoprene varies as a function of temperature. The pattern in Figure 3-6 also shows us that it would be unwise to include biogenic emissions (for which isoprene is a tracer) in the previously described comparisons of 6-9 am emission derived NMOC/NOx ratios with monitored ratios.

There are many reasons why it may be useful to perform previously described analyses on days with high ozone and contrast the results with other days. With respect to evaluating emissions, this may provide us with insight about whether there is something different about

emissions on days with high ozone vs. other days. Since our concern with emissions often focuses on high ozone days (e.g., for reasonable further progress calculations and for modeled attainment demonstrations), priorities may be greater to resolve discrepancies between emissions-derived estimates and monitored data on these days.

The graph shown in Figure 3-7 contrasts ozone observed on an episode day vs. mean observations for that month (Bigler-Engler et al.). Similar graphs in which other PAMS species are plotted could be used to identify possible discrepancies in average emissions estimates (often used in emissions models) vs. what appears to be consistent with observations on a limited number of episode days. Figure 3-8 plots an observed relationship between midday isoprene levels and temperatures, suggesting that inclusion of a strong temperature dependency in the emissions factor for biogenic emissions of that species is likely to be valid (Fehsenfeld et al.). Similar comparisons could be undertaken for tracers of other, anthropogenic sources.

3.4   EXAMPLE OF INVENTORY EVALUATION FOR LAKE MICHIGAN INVENTORY

Data collected during the 1991 Lake Michigan Ozone Study was the basis for comparison of the emissions inventory and ambient concentration ratios of NMOC/NO$_x$, and NMOC/CO for Chicago, Gary, and Milwaukee (Korc et al., 1993). Comparisons of 7-9 a.m. ratios for two ozone episodes (June 25-28 and July 16-18) showed that the ambient ratios were generally higher than the inventory ratios. The relative individual NMOC species compositions of the ambient and emissions inventory data were also examined. Table 3-3 shows the overall average ambient and emissions inventory relative compositions for individual species and species groups for the three cities during the two ozone episodes. The ambient relative compositions of the major groups of organic compounds are very similar at all three sites. The paraffin content in the ambient data is about 48 percent; the olefin content is about 10 percent; the aromatic content is about 22 percent; and the carbonyl content is about 4 percent.. The relative composition of the inventory is very similar at all three sites. However, the paraffin composition of the emissions inventory is about 5 to 10 percent lower than the corresponding ambient data at all three sites. Olefins are slightly higher than the ambient data at Gary and Milwaukee and are consistent with the ambient data at Chicago. The aromatic composition is significantly higher than ambient composition at all three sites and ranges from 27 percent at Milwaukee to 33 percent at Chicago. The carbonyl compound composition is significantly lower than the ambient data at all three locations; and the other species group composition is slightly higher than the ambient data at Chicago and Gary, and is consistent with the data at Milwaukee.

In response to this study, the Lake Michigan Air Directors Consortium (LADCO) reevaluated the emissions inventory and made several significant changes to the point, area, and mobile source figures. Speciation profiles and background assumptions were also revised.

LADCO then compared the revised emissions estimates to the ambient data and found improved agreement. Tables 3-4 and 3-5 show the computed ambient and emissions NMOC/NO$_x$ ratios both before and after the LADCO emissions inventory revision (Korc et al., 1993).

3.5 EXAMPLES USING MULTIVARIATE ANALYSES AND CHEMICAL MASS BALANCE (CMB)

Thus far, the focus of the discussion has been on various types of screening analyses for PAMS data which could serve as qualitative indicators for investigating certain assumptions underlying emissions estimates. This Section focuses on a series of analyses which has as its end product more quantitative estimates of the contributions that various source categories make to observed ambient measurements of ozone precursors. Although the end product of these analyses is quantitative, it is obtained through use of much subjective judgment. Therefore, we do not recommend using the outcome of these analyses to change emissions estimates unless the methodology for making the emissions estimates is also reexamined and the uncertainties in these procedures are consistent with the changes implied by the analyses of the ambient data. In short, although the results obtained with the techniques summarized in this section are quantitative, they should be used qualitatively to improve emissions estimates.

The Chemical Mass Balance (CMB) model (U.S. EPA, 1990a) can be used to provide quantitative source category contribution estimates to monitored data. This procedure uses distinct chemical species profiles for different source categories and then identifies the relative combination of contributions from each of the selected source categories which best explains the combination of species observed at the monitoring site. One key prerequisite for a CMB analysis is choice of the source species profiles. There are two approaches used for choosing source chemical profiles. The first is to select source categories and their corresponding species profiles from available local measurements of a source's emissions or to select profiles from a "library" of source chemical profiles. The latter approach is the simpler of the two. It may be preferred if one already has a good idea of the source categories which are likely to make important contributions and has confidence in the profiles which are used. The EPA's Air Emissions Species Manual (U.S. EPA, 1990b) documents default species profiles for many sources of VOC. When available, species profiles measured in recent local field studies should be used instead.

Although species profiles for many types of sources are included in the Air Emissions Species Manual, some of the data may be outdated or not applicable to the area in which we are seeking to corroborate emissions estimates. Further, one could argue that using default species profiles for the CMB which are the same as those underlying the inventory is not a completely rigorous corroboration of the inventory. Thus, the second approach for choosing chemical source profiles for use in the CMB is to try to use the ambient observations themselves to derive

source category profiles. Methods to implement this second approach can be broadly characterized as "multivariate analyses".

In Sections 3.5.1 and 3.5.2, we illustrate how PAMS data are useful in applying the chemical mass balance model and corroborating emissions estimates using examples in Atlanta and Southern California. [Additional information on the CMB technique may be found in U.S. EPA, 1987 and U.S. EPA, 1990a].

3.5.1 Example of Inventory Evaluation in Atlanta

Atlanta has been the focus of many receptor modeling studies in the past decade.   CMB has made possible a new approach to comparing emissions inventories with ambient data using CMB calculations (Conner). This new approach make use of <u>ranges</u> of source estimates obtained from the ambient data, which can be used to deal with some of the inherent difficulties of comparing inventories with ambient data. Table 3-6 compares the CMB output with emissions inventory data obtained from the Georgia Department of Natural Resources. The comparison is qualified "by the fact that the CMB results reflect mostly daytime (hours 8-18) conditions, while the inventory represents 24-hour average emissions."

As seen in Table 3-6, the biogenic mass was accounted for using several different methods. The biogenic portion of the CMB estimate was set equal to the biogenic portion of the emissions inventory; then it was set equal to the isoprene percent; then set equal to the 'unexplained' percent; and then also set equal to zero. The inventory highway mobile source estimate tends to be smaller than the <u>minimum</u> ambient data-derived highway mobile source estimate, and the inventory area plus point source estimate tends to be larger than the <u>maximum</u> ambient data-derived estimate for the data set examined." Such a comparison is useful in evaluating the inventory, but in this case, only limited confirmation of the inventory can be gleaned from the CMB-based analysis; other analyses would be needed to support further evaluation of the inventory.

3.5.2 Example of Inventory Evaluation in Southern California

The Southern California Air Quality Study (SCAQS) was conducted in summer and fall 1987 to gain a better understanding of the causes of excess pollution concentrations in California's South Coast Air Basin (SoCAB). The SCAQS data was used to validate the use of CMB for NHMC source apportionment (Fujita et al.). One of the goals of their study was to reconcile source contribution estimates from the CMB with existing emissions inventory estimates. Table 3-7 shows the mean source contribution estimates for all sites combined by season and sampling period for the three motor vehicle source categories versus all other source categories in comparison to the corresponding SCAQS basin wide day-specific emissions

inventory data for August 27, 1987 and December 10, 1987 (Fujita et al.).

Fujita et al. noted that "the larger calculated contributions of vehicle exhaust and evaporative emissions were consistent with recent studies that suggest that the motor vehicle hydrocarbon emissions inventories for motor vehicles have been substantially underestimated".

Fujita et al. concluded from their evaluation that "the CMB application and validation protocol developed for PM-10 source apportionment is applicable to the validation of CMB for NMHC source apportionment". They suggested, however, that additional source profiles be designed specifically for receptor modeling. They noted that "the attribution of source contributions among the motor vehicle source categories was found to be highly sensitive to the choice of fitting species and to the relative abundance of combustion byproducts in the exhaust profile, which vary with emissions control technology, level of vehicle maintenance, and operating mode." They recommended the creation of site-specific vehicle exhaust profiles.

3.6   CASE STUDY - EXAMPLE OF INVENTORY EVALUATION IN HOUSTON, TEXAS

This case study highlights a comprehensive review of the emissions inventory in Houston TX. This example illustrates how several different techniques can be combined to build a thorough evaluation of an inventory for ozone precursors. The techniques include: ambient and emissions-derived NMOC/NOx; relative compositions of hydrocarbon groups using both ambient and emissions derived data; and CMB analysis.

NMHC/NO$_x$ ratios were compared for two Houston sites in summer 1993 (Korc et al., 1995). Emissions inventory data were delineated to 5 different grid areas surrounding the site using two different allocation approaches. (One approach allocated emissions inventory data from upwind grid cells with a weighting function of 1; the other allocated emissions inventory data from upwind grid cells with a weighting function defined as the inverse of the distance between the ambient monitoring site and the centroid of each grid cell.) As seen in Tables 3-8 and 3-9, the ambient ratios were always significantly higher than the corresponding emissions ratios (Korc et al., 1995). At Galleria, the ambient ratios were about 2 to 6 times the emissions ratios; at Clinton, the ambient ratios were approximately 2.5 to 4 times the emissions ratios. Galleria represents a major urban source dominated by mobile emissions and Clinton represents a major industrial location.

In the report, Korc also made comparisons between the relative ambient and emissions compositions. Figure 3-9 shows comparisons of the August 19 day-specific, August 17-20 episode specific average, and August and September weekdays median 0600 CST ambient- and August 19 emission-derived relative composition of paraffins, olefins, aromatic compounds and

"other" species groups at Clinton (Korc et al.,, 1995). Note that the ambient-derived and emissions inventory relative proportions of paraffins and olefins are rather comparable, the emissions inventory estimates for aromatics is significantly higher than the ambient-derived estimates, and the emissions inventory "other" species estimate is much lower than ambient-derived figures. a similar chart comparing the relative individual species compositions (top 35 species) for the same four types of estimates is shown for Galleria in Figure 3-10 (Korc et al.,, 1995).

The data in Figure 3-10 show that the emissions inventory toluene and n-butane moleC percents of NMHC were significantly higher in the emissions inventory estimate than the ambient derived percents and the relative isopentane, ethane, and propane moleC percents were significantly lower in the emissions inventory (Korc et al.,, 1995). Evaluating the same set of ambient data, Lu and Fujita (1995) compared hourly CMB and emissions inventory source contribution estimates (as percents of NMHC) for the three source categories: mobile, biogenic, and miscellaneous. As seen in Figures 3-11 and 3-12, the mobile source emissions inventory diurnal estimates were always lower than the CMB derived estimates at Clinton; at the Galleria site the two sets of estimates were closer and the emissions inventory estimates exceeded the CMB figures for 10 of the 24 hours. The biogenic emissions inventory estimates were always higher than the CMB figures at both locations.   The miscellaneous source emissions inventory diurnal estimates for Clinton exceeded the CMB estimates except for hours 2-8 p.m. when the two estimates were either very close or the CMB was slightly higher. At Galleria the situation was almost reversed, with the CMB estimates exceeding the emissions inventory data all hours but 8-11 a.m.

Based on their review, Sonoma Technologies, Inc. concluded that significant discrepancies between the ambient data and the emissions inventory still exist. Thus, they made the following recommendations to improve the inventory:

- NMHC and NO_x emissions estimates should be reviewed.   Preliminary results indicate that the ambient-derived $NMHC/NO_x$ ratios are significantly higher than the emissions-derived $NMHC/NO_x$ ratios. These discrepancies suggest that the absolute amounts of NMHC and/or NO_x emissions were not estimated accurately. Thus, they recommended that an investigation of the possible biases in the NMHC and NO_x emissions inventories be performed. a series of bottom-up evaluations of the major components of the inventory are needed. These should be followed by further top-down evaluations.

- Speciation profiles should be reviewed. The discrepancies between ambient and emissions NMHC compositions and the significant overestimation of toluene in the inventory suggest that some of the assigned organic compound source composition libraries were not representative of some source category in the region, improper speciation profiles

were assigned, and/or the absolute amounts of NMHC emissions were not estimated accurately. Further, the significant overestimation of n-butane and toluene and the significant underestimation of isopentane in the emissions inventory suggest that the speciation profiles used for mobile sources may not reflect current gasoline reformulations and should be reviewed.

- Diurnal profiles should be reviewed. In particular, the significant overestimation of n-butane in the emissions inventory early in the morning suggests that the diurnal profiles used for motor vehicle evaporative emissions may not be representative and should be reviewed.

- Biogenic emissions estimates should be reviewed. In particular, the significant overestimation of isoprene in the emissions inventory early in the morning suggest that the biomass data, land use data, and/or the algorithm used to estimate isoprene emissions may not be accurate and should be reviewed.

3.7 CONCLUSIONS

PAMS data can provide useful information to evaluate emissions inventories. It can provide a general idea of the relative importance of certain compounds in the inventory that can suggest the need for improved speciation of the data. Also, it can provide information related to the spatial or temporal resolution of the inventory. It has been used to identify missing components of the inventory and gross over/under calculations of the inventory based on emissions factors.

Several techniques and analytical tools are available to evaluate the inventory.   Simple techniques such as time series analysis, diurnal patterns and pollution roses can be augmented by Chemical mass balance and other multivariate techniques. Use of multiple techniques can provide more useful information than relying on one or two methods. Also, PAMS data provides a unique opportunity to compare the model-estimated species concentrations with ambient measurements of these species at the time of day that the measurements were taken. However, photochemical models have not yet progressed to the point where the results for individual species are tracked along with the transformation chemistry.

Several areas of the US have used PAMS data to evaluate the emissions inventory. Examples from the Texas Gulf Coast, Atlanta, Houston, Atlanta, Los Angeles and the Great Lakes have been shown.   Additional analyses have been undertaken in Hartford and other cities. The real value of such analyses is just now being realized as more PAMS networks develop validated data sets.

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Emission Inventory Areas Surrounding a Site


```
---- 1-cell
——  9-cell
— — 25-cell
▬▬ 81-cell
---- Quadrant
```
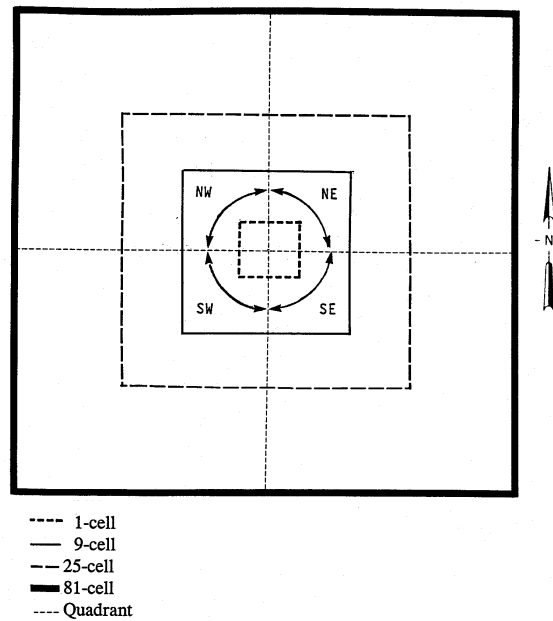
Figure 3-1. Schematic illustration of 1-cell, 9-cell, 25-cell, and 81-cell areas surrounding a site, and the upwind quadrants of the 81-cell area.
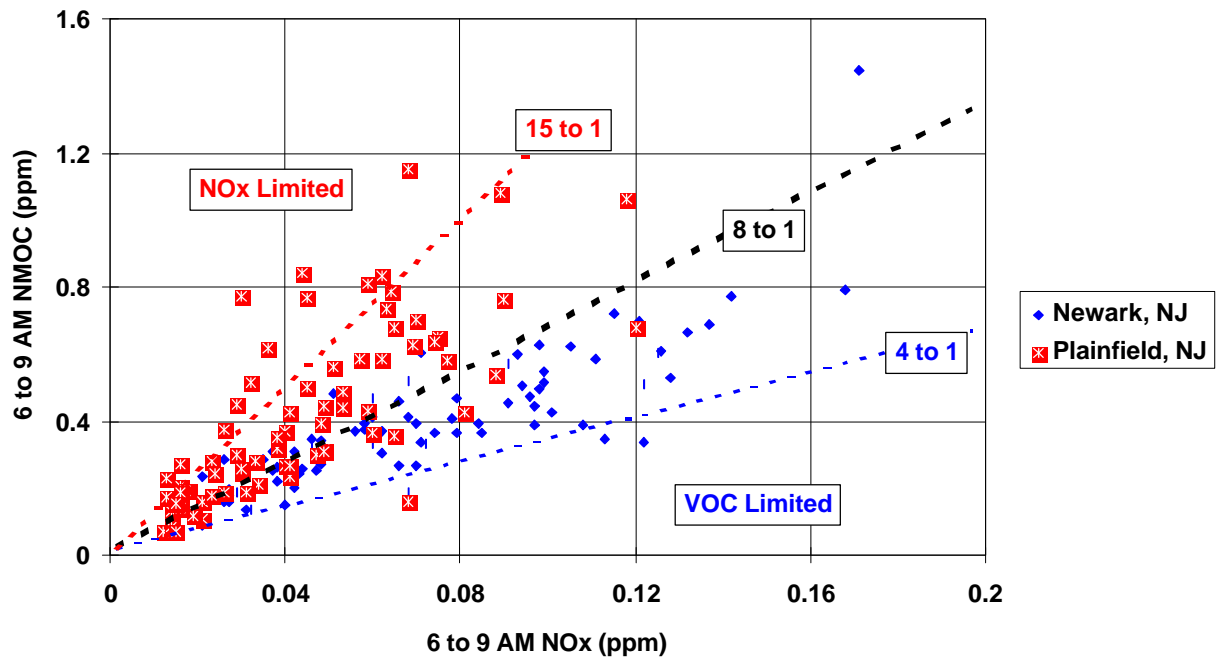
Figure 3-2. Morning NMOC:NOx Ratios at Urban and Suburban New Jersey Sites, Summer, '93
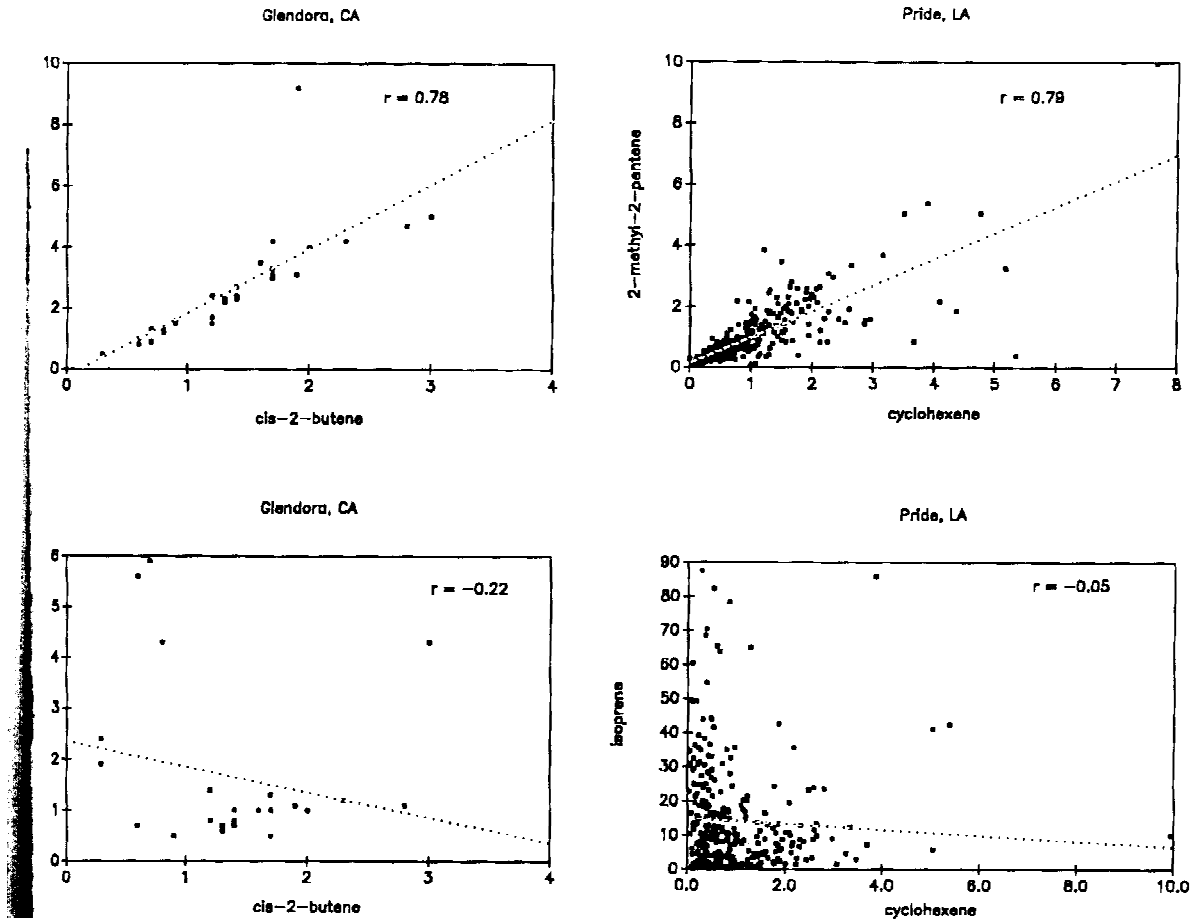
Figure 3-3. Scatterplots of the concentrations (ppbC) of trans-2-pentene, cis-2-butene, cyclohexene, 2-methyl-2-pentene and isoprene as observed in Pride, Louisiana and Glendora, California

POLLUTION ROSE
June 27 - July 06
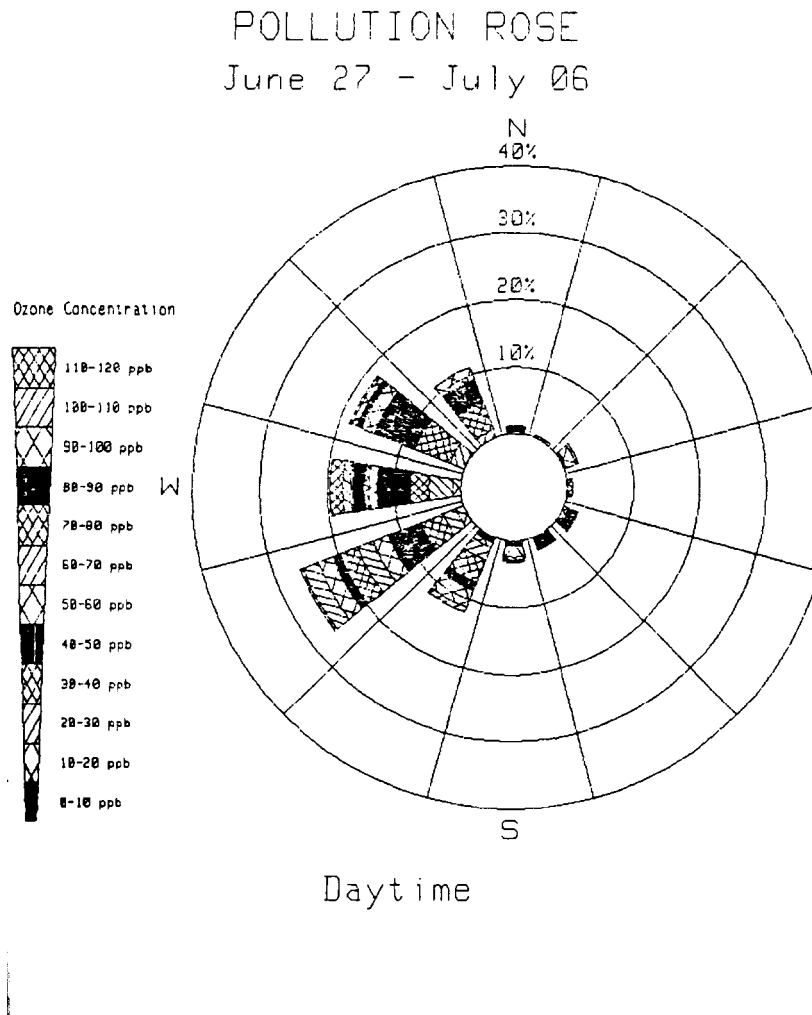
Figure 3-4. Daytime pollution (ozone) roses in a summer period.

Diurnal Profiles for
HOUSTON - Galleria

Weekday   Weekend

Acetylene   Acetylene

Ethylene   Ethylene

Ethane   Ethane
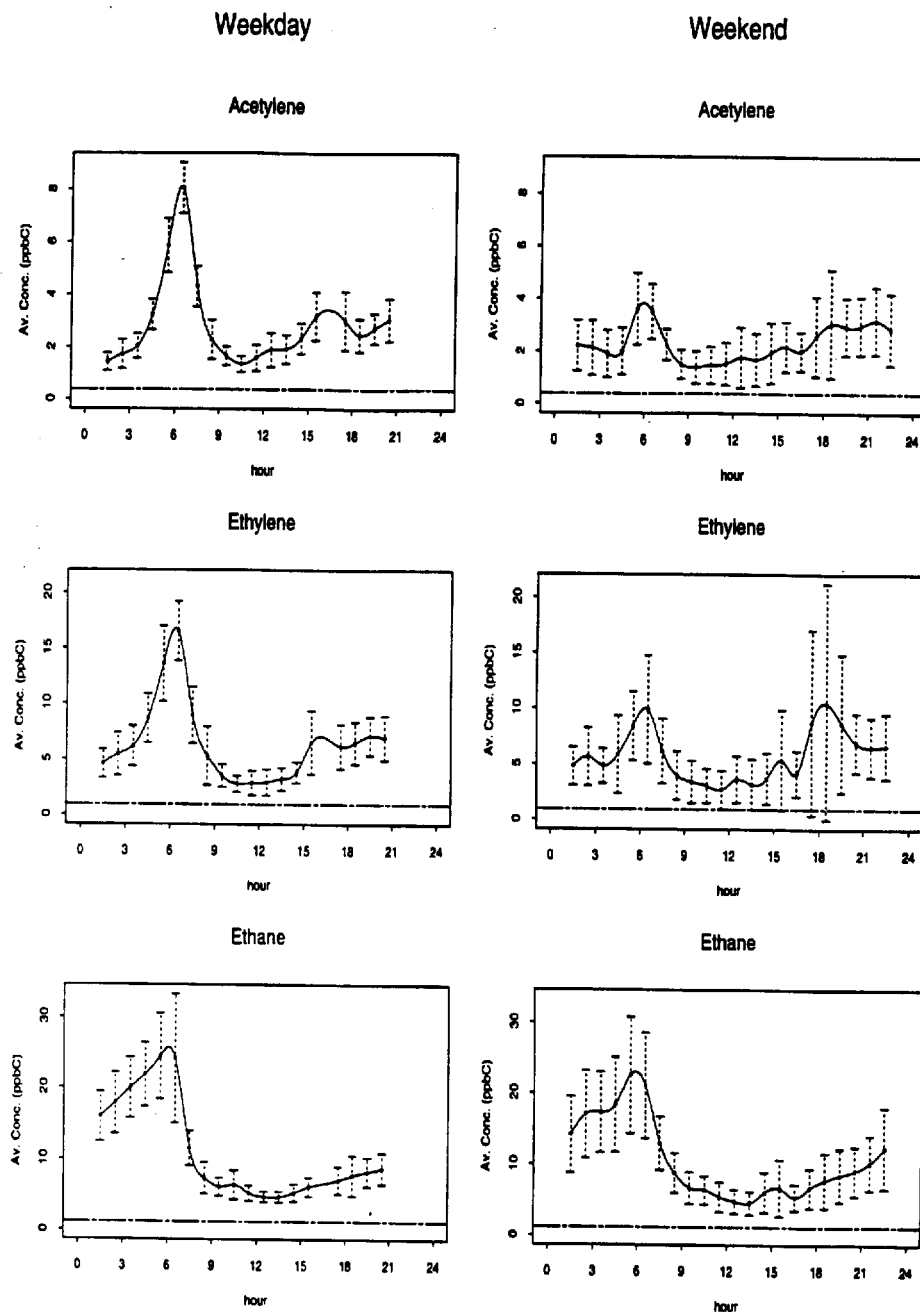
Figure 3-5.

Diurnal Profiles for
HOUSTON - Galleria

Weekday   Weekend

Isoprene   Isoprene

Benzene   Benzene

Toluene   Toluene
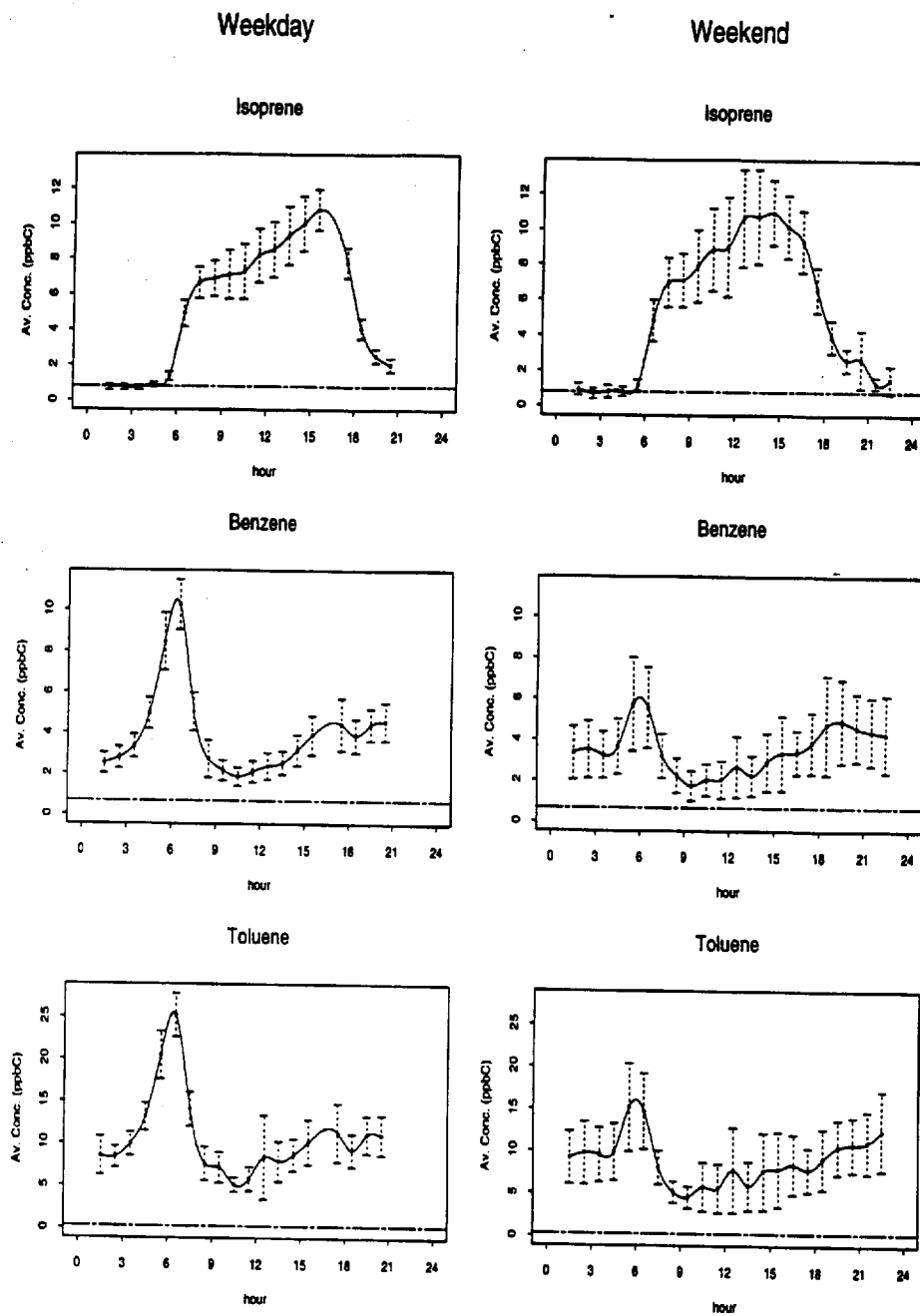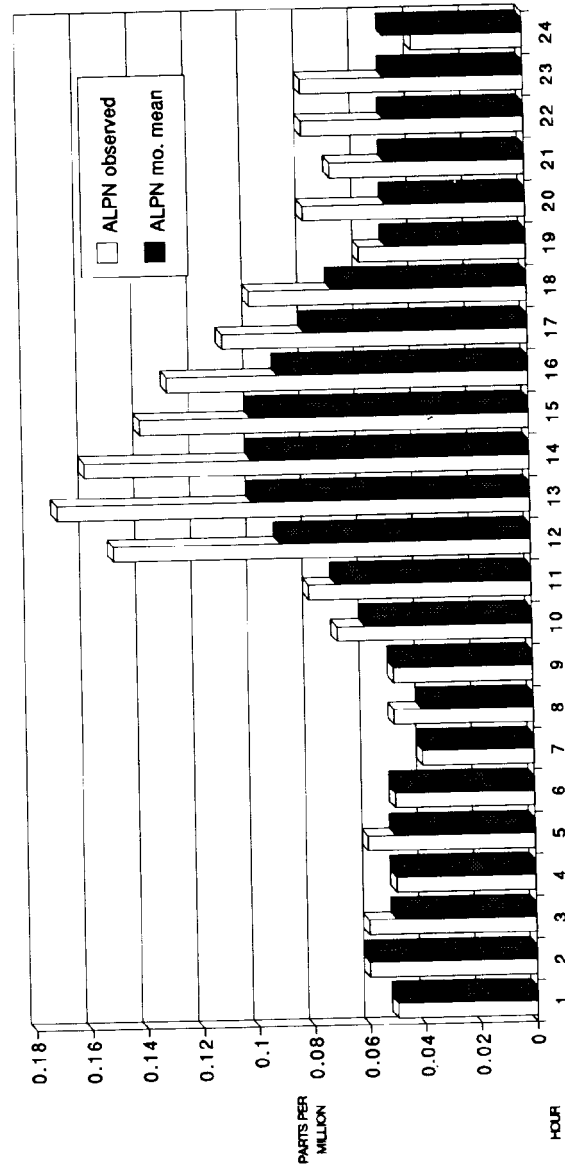
Figure 3-6.

Figure 3-7. Hourly Ozone versus Mean, Alpine 9/26/89.

20
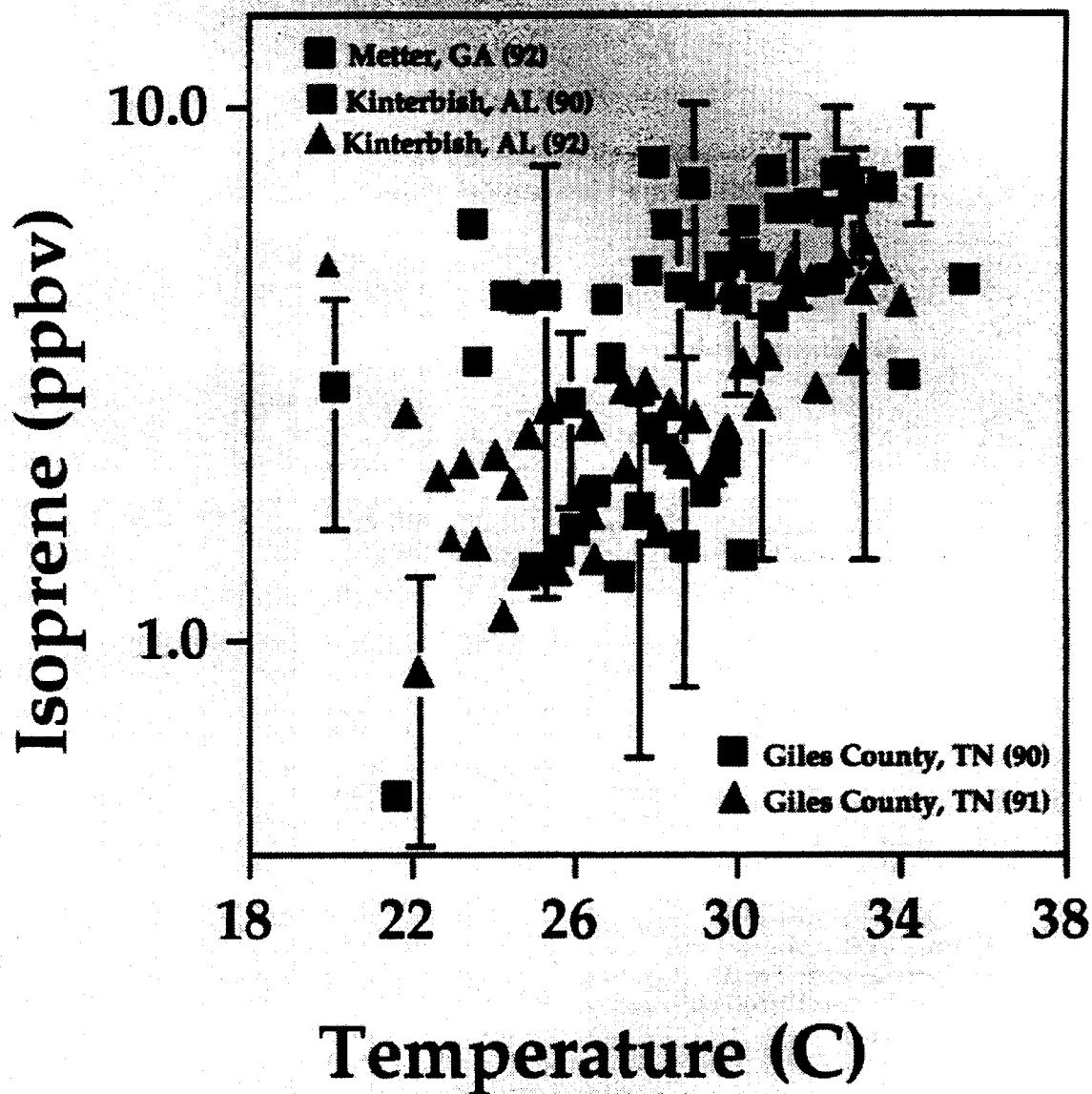
Figure 3-8. Plot of isoprene mixing ratio versus temperature taken from air concentration measurements during summer (June-August) during the daytime hours. In these plots the data for each measurement set was divided into twenty subsets, each containing 5% of the data points. The vertical bars indicate the standard deviation in the measurements for a few selected data subsets from these measurements. The measurements were made at Kinterbish, Alabama during the summers of 1990 (squares) and 1992 (triangles); at Giles County, Tennessee during the summers of 1990 (squares) and 1991 (triangles); and at Metter, Georgia in 1992 (squares).
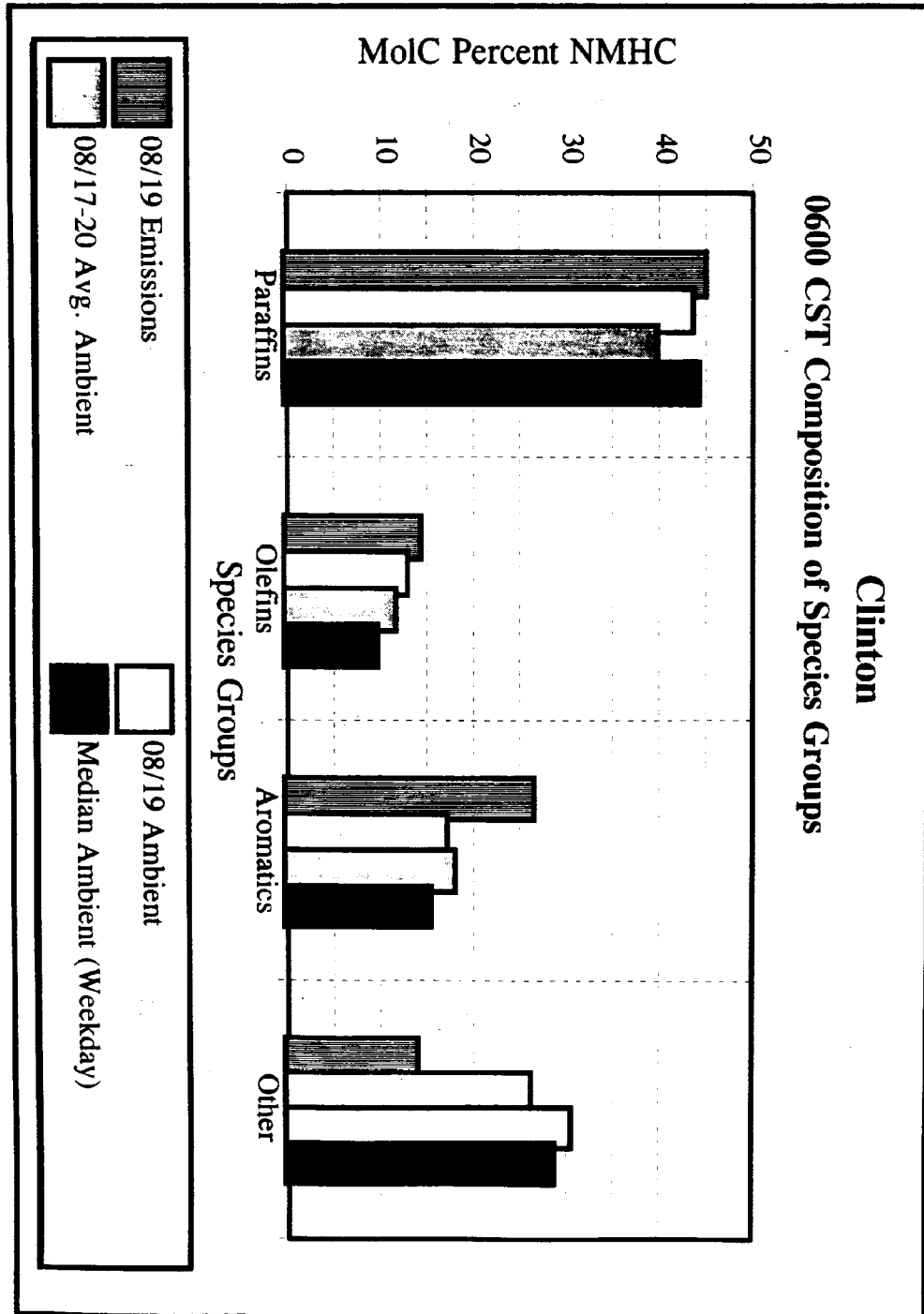
Figure 3-9. Houston (Clinton Site) - Comparisons of 0600 CST Ambient and Total Emissions-Derived Species Group Compostion Estimates for the 81-Cell Area Surronding the Clinton Site, 1993

Figure 3-10.

Galleria

Ambient and Emission Inventory Composition

0600 CST
Mobile Sources
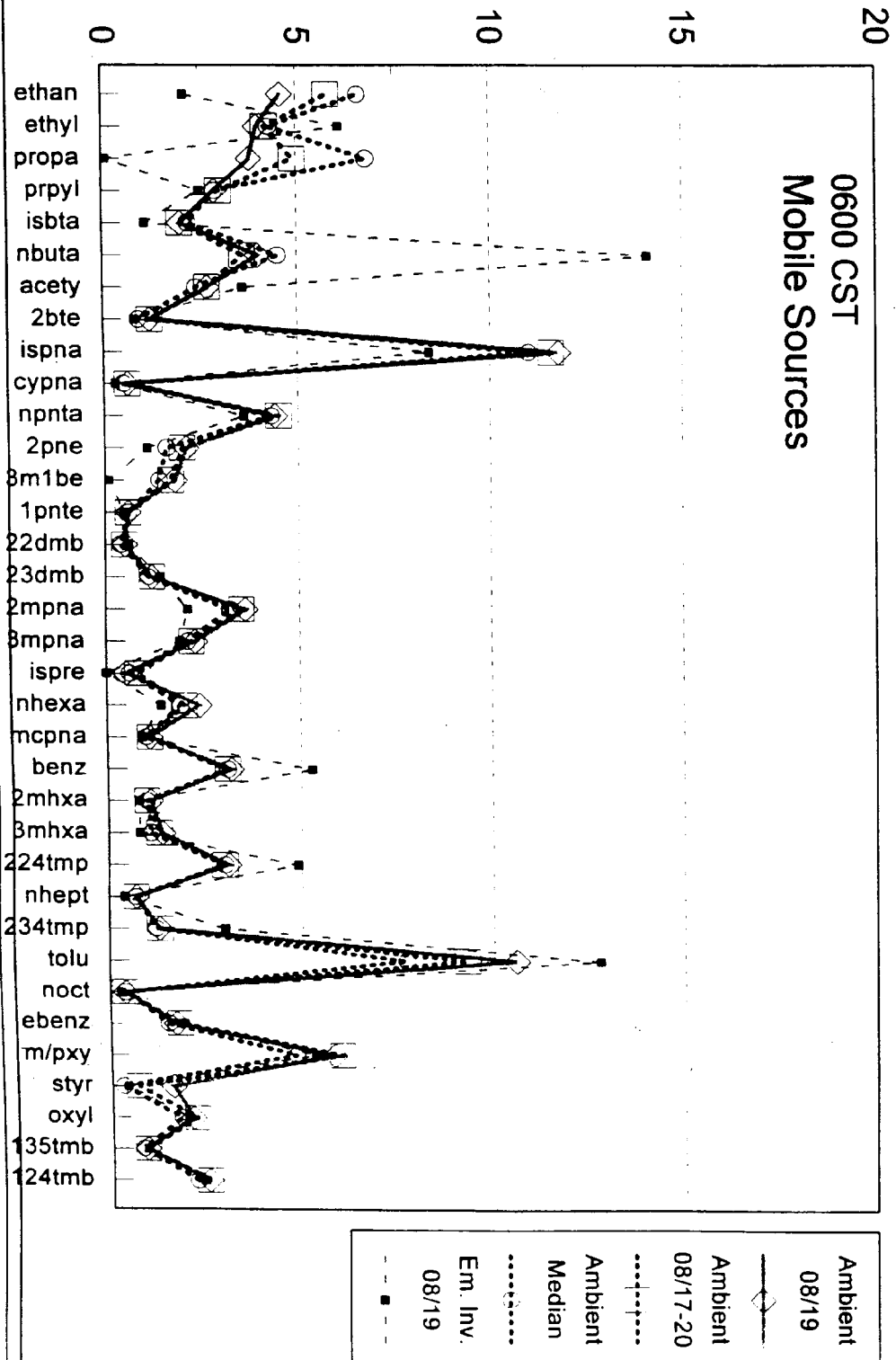
Figure 3-11.　Houston (Clinton Site) - Comparisons Between CMB Results and Emission Inventories,
August 19, 1993

Comparisons Between CMB Results and Emission Inventories
for August 19, 1993 at Clinton
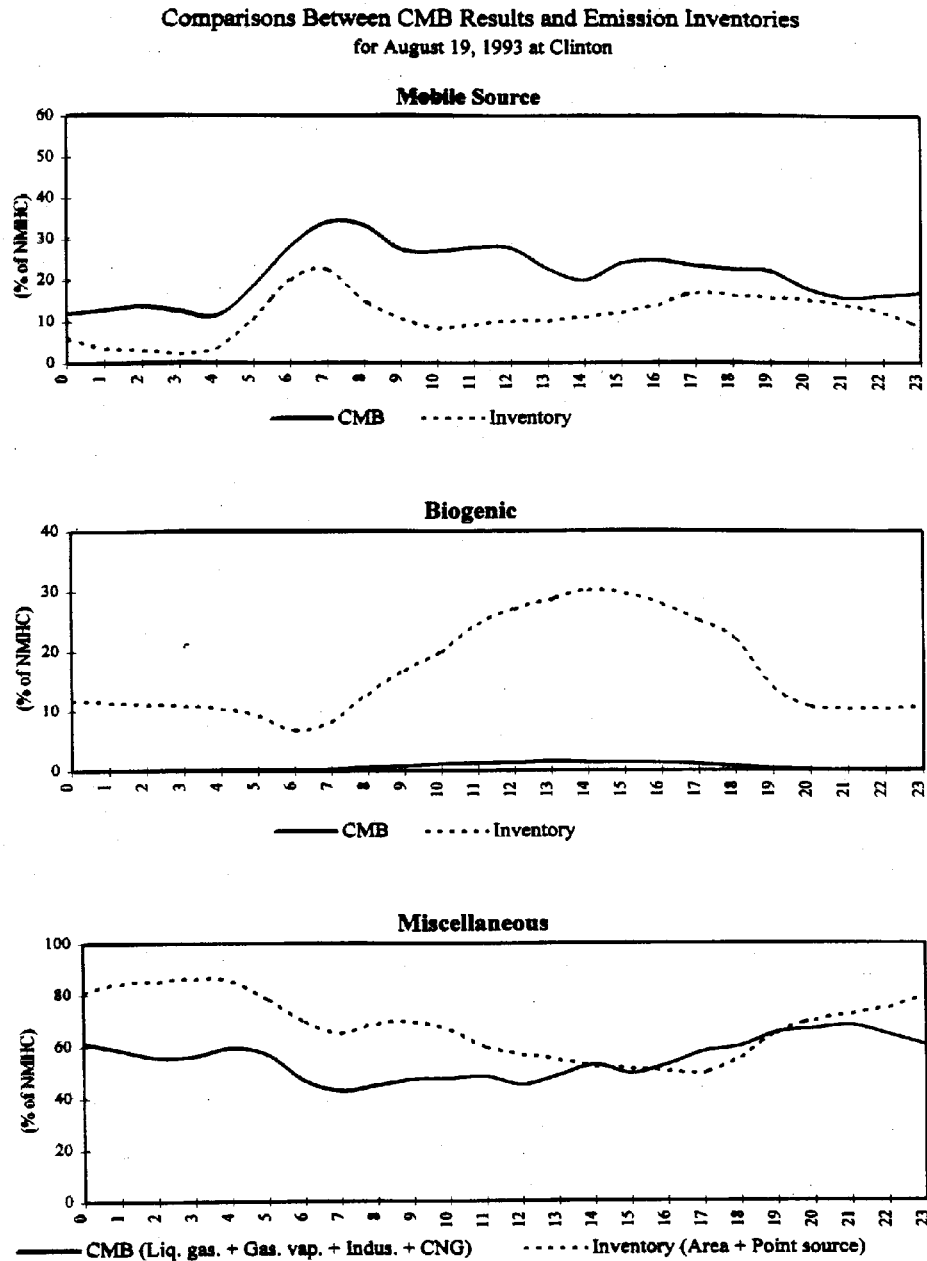
Source: Lu and Fujita, 1995

Figure 3-12. Houston (Galleria Site) - Comparisons Between CMB Results and Emission Inventories,
August   19, 1993

Comparisons Between CMB Results and Emission Inventories
for August 19, 1993 at Galleria

Mobile Source

CMB ......Inventory

Biogenic

CMB ......Inventory

Miscellaneous

CMB (Liq. gas. + Gas. vap. + Indus. + CNG) ......Inventory (Area + Point source)
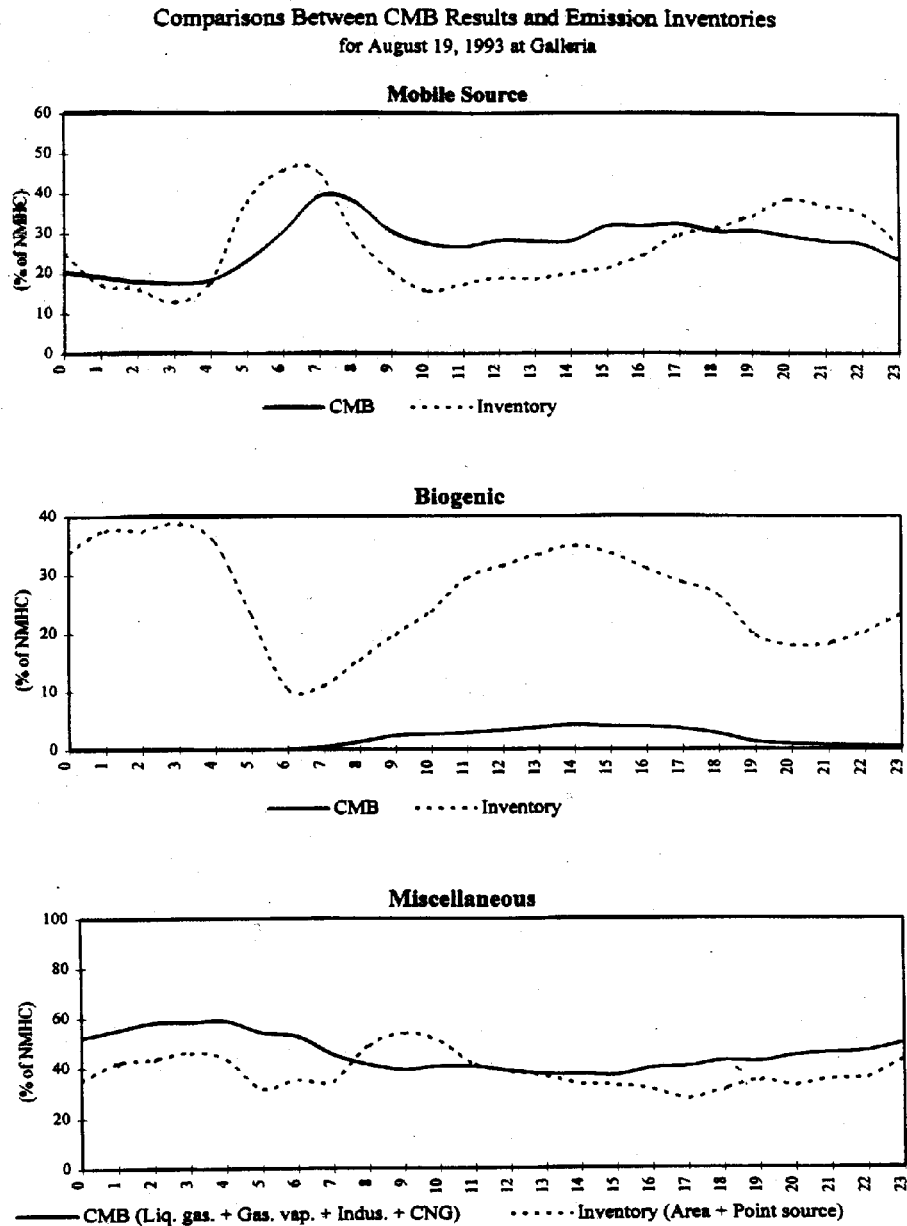
Source: Lu and Fujita, 1995

Table 3-1. Emission Factor Representativeness and Application Issues

| Problem	Discussion
Unrepresentative Factors and Models	There are over 9,000 processes defined in FIRE, the Factor Information and Retrieval System, but many processes are not represented for each and every pollutant. Thus, one might choose a factor for a "similar" process without knowing whether it will be entirely appropriate for the task at hand. Similarly, the factor may not be parametized all key process variables that could affect emissions, e.g., temperature, pressure, maintenance, emission control measures.
Control Efficiency	The design criteria of air pollution control equipment affect the resulting emissions. Design criteria include such items as the type of wet scrubber used, the pressure drop across a scrubber, the plate area of an electrostatic precipitator, and the alkali feed rate to an acid gas scrubber. Operation and maintenance of control devices can substantially effect emissions.
Within-source Variability	Short-term emissions from a single specific source often vary significantly with time (i.e., within-source variability) because of fluctuations in process operating conditions, control device operating conditions, raw materials, ambient conditions, and other such factors. Emission factors generally are developed to represent long-term average emissions, so testing is usually conducted at normal operating conditions.
Variability Between Sources	Average emissions differ significantly from source to source and, therefore, emission factors frequently may not provide adequate estimates of the average emissions for a specific source. The extent of between-source variability that exists, even among similar individual sources, can be large, depending on the specific process, control system, and pollutant.
Spatial Resolution	Often, the activity parameter data that must be input to use on emission factor or model is not readily available on a finely gridded scale. Most emissions models grid the county-level data based on an appropriate surrogate indicator such as population, land use, or digitized highway data. Obviously, the better the surrogate, the more accurate the gridded emissions will be that can be used for comparison to the ambient data. The acquisition of high-resolution surrogate data can be very difficult and extremely costly. Ambient measurements can help determine whether appropriate resolution has been attained.
Temporal Resolution	Photochemical models are often run for specific dates. However, emission factors are not intended to be representative of specific timeframes and are inherently less reliable under such demands. Thus, it is very important to evaluate date-specific emissions data with all available tools, including ambient data. Resolution of temporal issues is difficult because ambient measurements are generally collected on an hourly basis and most emission inventory estimates are defined on a daily or annual basis. Also, it is difficult to resolve emissions from batch processes with ambient data.
Speciation Problems	A problem particular to VOC emission estimates is that the VOC emission must be speciated by a preprocessor before it is used in a photochemical model and errors can be made that offset the photochemistry calculations. Unfortunately, inventories only contain unreacted species, or Ozone precursors, and current photochemical models track groups of species that may be associated with more than one source. Thus, these comparisons can currently be made only for unreacted (or possibly for slowly reacting) species.
Missing Sources	The importance of using ambient measurements to reveal missing sources or source categories became apparent as early as 1976 when the microscopic analysis of ambient particulate matter samples revealed much more soil-related particles than were accounted for by the emissions inventory. (Bradway and Pace, 1976)

Table 3-2. Commonly Used Tracers for Ozone Precursors (Stoeckenius et al., 1994 a)

Compound	Major Source	Comments
Numerous VOC's	Specific industrial processes	May be identified from emissions of various industrial facilities
α- and β-pinene	Biogenic emissions	Highly reactive, measurement difficulties, also present in consumer products such as air fresheners
Benzene	Motor vehicle exhausts	Also present in evaporative emissions and numerous combustion processes. Useful in developing upper bound estimate of motor vehicle exhaust
Butane	Gasoline evaporative emissions	Accounts for roughly 35% of motor vehicle evaporative emissions
Ethane	Natural gas use/leakage	Measurement difficulties as noted for acetylene
Isobutane	Consumer product emissions	Has replaced chlorofluorocarbons in most consumer aerosol products
Isoprene	Biogenic emissions	Highly reactive but most frequently used for tracing biogenic emissions
Propane	Liquefied petroleum gas (LPG) use, refinery emissions, oil & gas production	Difficult to use as simple tracer if more than 1 type of source in area
Toluene	Motor vehicle exhaust, surface coating processes such as those involving solvent-based paints	Present in characteristic ratios in motor vehicle exhaust; excess beyond that attributed to surface coating processes and printing

Table 3-3.   Average NMOC weight percent of the individual organic species in the first LMOS emission inventory and in ambient air at Gary, Chicago and Milwaukee, 1991.

Species	Gary		Chicago		Milwaukee	
	Ambient* %NMOC	Emissions %NMOC	Ambient %NMOC	Emissions %NMOC	Ambient* %NMOC	Emissions %NMOC
Paraffins	47	39	49	40	50	45
Acetylene	2.5	0.8	2.3	1.0	2.7	1.2
Ethane	5.7	0.7	2.9	1.1	3.5	0.9
Propane	3.9	0.2	3.1	0.5	3.7	0.2
n-Butane	4.0	8.4	5.0	9.0	6.3	13.2
i-Butane	1.9	2.7	2.1	1.4	2.4	1.0
n-Pentane	2.8	2.3	3.6	2.4	3.4	3.5
Branched C5	9.5	5.7	9.9	6.0	10.4	7.0
Branched C6	6.2	3.4	6.1	3.1	6.4	4.0
Metylcyclopentane	0.9	0.5	1.1	0.4	1.1	0.6
n-Hexane	1.4	1.6	2.3	1.0	1.7	1.5
Branched C7	3.1	2.1	3.4	2.2	3.7	2.5
Cyclic C7	0.3	2.3	0.5	2.6	0.5	1.8
n-Heptane	0.6	2.4	1.0	2.8	0.9	1.7
Branched C8	3.0	4.7	3.8	4.9	4.1	5.3
n-Octane	0.6	0.3	0.5	0.3	0.4	0.2
n-Nonane	0.3	0.3	0.4	0.3	0.4	0.2
Olefins	9	11	10	10	9	12
Ethene	3.1	2.7	4.7	2.5	3.8	2.9
Propene	0.8	0.8	0.9	1.0	1.0	1.1
Terminal C4 olefins	0.8	0.7	0.7	0.3	0.7	0.4
Internal C4 olefins	0.9	0.8	1.0	0.7	1.3	0.8
Terminal C5 olefins	0.3	0.9	0.5	0.7	0.4	0.9
Internal C5 olefins	1.1	1.6	2.0	1.6	1.3	2.2
Cyclopentene	0.4	0.5	0.3	0.2	0.3	0.3
Isoprene	1.4	1.0	0.2	0.1	0.4	0.3
Terminal C6 olefins	0.1	0.9	0.1	1.1	0.3	1.5
Internal C6 olefins	0.1	1.1	0.1	1.5	0.1	2.0
Aromatics	22	31	23	33	20	27
Benzene	2.4	2.6	2.6	2.9	2.7	3.0
Toluene	7.1	14.6	8.4	19.9	7.7	12.9
Ethylbenzene	1.2	1.5	1.3	1.1	1.1	1.3
Styrene	0.6	0.1	0.4	0.5	0.5	0.2
Trimethylbenzenes	2.9	2.6	3.2	1.6	2.7	2.3
Propylbenzenes	0.5	0.6	0.9	0.3	0.4	0.4
Xylenes	7.3	9.3	6.3	6.3	5.0	7.0
Carbonyls	4	1	3	1	3	1
Formaldehyde	2.4	0.4	2.0	0.6	2.0	0.4
Acetaldehyde	1.6	0.2	0.9	0.3	1.0	0.2

* NMOC percents correspond to June 26, July 16, and July 18, 1991.

Table 3-4.   Lake Michigan Area - Ambient Versus Original Set of EI NMOC/NO$_x$ Ratios, 1991

Site	Ambient NMOC/NO$_x$	Emission NMOC/NO$_x$	Ambient/EI
Gary[a]	5.3	4.3	1.2
Chicago	4.8	2.6	1.9
Milwaukee[a]	6.4	4.2	1.6

[a] Ambient NMOC/NO$_x$ ratios correspond to June 26, July 16 and 18, 1991

Table 3-5.   Lake Michigan Area - Ambient Versus Revised Set of EI NMOC/NO$_x$ Ratios, 1991

Site	Ambient NMOC/NO$_x$[b]	Emission NMOC/NO$_x$	Ambient/EI
Gary[a]	4.8	5.0	1.0
Chicago	4.7	3.6	1.3
Milwaukee[a]	6.4	3.8	1.7

[a] Ambient NMOC/NO$_x$ ratios correspond to June 26, July 16 and 18, 1991

[b] Ambient NMOC/NO$_x$ with background correction

Table 3-6. CMB Vs Emission Inventory Source Contribution Estimates, 1990

Summary of CMB Results*	Summary of Emission Inventory

Assume biogenic % = % reported in inventory (16.8%):
                                MIN. MAX.
HIGHWAY MOBILE SOURCES: 61% 75%
POINT + AREA SOURCES: 8% 23%
 	
Assume biogenic min. % = isoprene % (1.9%):
                              MIN. MAX.
HIGHWAY MOBILE SOURCES: 71% 89%
POINT + AREA SOURCES: 9% 27%
 	
Assume biogenic max. % = % unexplained (47.4%):
                              MIN. MAX.
HIGHWAY MOBILE SOURCES: 41% 51%
POINT + AREA SOURCES: 5% 15%
	Including Biogenics:
	
	HIGHWAY MOBILE SOURCES:
	56.0%
	POINT + AREA SOURCES:
	27.2%

Assume no biogenics: MIN. MAX. **HIGHWAY MOBILE SOURCES:** 73% 91% **POINT + AREA SOURCES:** 9% 27%	Excluding Biogenics: **HIGHWAY MOBILE SOURCES:** 67.3% **POINT + AREA SOURCES:** 32.7%

* Results presented as percent of total apportioned NMOC (sum of source estimates).

period	vehicle exhaust	liquid gasoline	gasoline vapor	nonMV
Summer Study				
CMB				
0700-0800	50.5	16.6	10.9	22.1
1200-1300	53.7	14.0	11.2	21.0
1600-1700	48.8	11.4	10.3	29.5
emission inventory				
0600-0800	49.5	9.1	5.6	35.9
1100-1300	21.9	5.5	3.4	69.2
1500-1700	30.4	7.3	8.0	54.3
daily total	28.3	6.3	4.5	59.0
Fall Study				
CMB				
0700-0800	67.9	14.5	6.8	10.8
1200-1300	53.7	14.0	11.2	21.0
1600-1700	56.2	14.7	9.5	19.6
emission inventory				
0600-0800	62.1	8.8	2.9	26.2
1100-1300	26.4	6.0	3.1	64.5
1500-1700	38.1	7.2	6.4	48.3
daily total	37.4	6.8	3.5	52.3

Table 3-7.   South Coast Air Basin - CMB Vs Emission
Inventory Source Contribution Estimates, 1987

Table 3-8.   August 19, 1993 0500-0800 CST ambient-and emissions derived NMHC/NO$_x$ ratios for total inventory emissions at Galleria.

Time (CST)	Emission NMHC/NO$_x$						Ambient NMHC/ NO$_x$
	1-Cell	9-Cell	25-Cell	81-Cell	Quadn[a]	Quadw[b]	
5	1.2	1.4	1.5	1.7	2.2	2.0	12.1
6	1.2	1.4	1.5	1.5	1.7	1.7	9.2
7	2.0	2.4	2.7	2.6	2.8	2.7	5.7

[a] Linear combination of emission inventory data from upwind grid cells with a weighing function of 1.
[b] Linear combination of emission inventory data from upwind grid cells with a weighing function defined as the inverse of the distance between the ambient monitoring site and the centroid of each grid cell.

Table 3-9.   August 20, 1993 0100-0800 CST ambient-and August 19, 1993 0100-0800 CST emissions-derived NMHC/NO$_x$ ratios for total inventory emissions at Clinton.

Time (CST)	Emission NMHC/NO$_x$						Ambient NMHC/ NO$_X$
	1-Cell	9-Cell	25-Cell	81-Cell	Quadn[a]	Quadw[b]	
1	1.6	2.6	2.0	2.7	1.9	2.0	10.5
2	1.6	2.6	2.0	2.7	1.5	1.4	11.4
3	1.6	2.5	2.0	2.7	1.5	1.4	8.6
4	1.6	2.4	1.9	2.4	1.3	1.3	7.1
5	1.7	2.3	1.9	2.2	1.5	1.5	5.3
6	1.5	2.1	1.7	1.9	1.3	1.3	4.9
7	1.7	2.5	2.2	2.6	2.1	2.0	4.8

[a] Linear combination of emission inventory data from upwind grid cells with a weighing function of 1.
[b] Linear combination of emission inventory data from upwind grid cells with a weighing function defined as the inverse of the distance between the ambient monitoring site and the centroid of each grid cell.

APPENDIX A. VOC SOURCE APPORTIONMENT/RECEPTOR MODELING STUDIES

No. / Study Name								
Researchers, Affiliation, Date	**Location**	**Time**	**Sponsor**	**Approach**	**No. of profiles**	**No. of fitting species**	**Conclusions**	**Comments**
A Chemical Mass Balance for Volatile Organics in Chicago								
O'Shea and Scheff, Ill. Inst. of Tech., 1988	Chicago (1 site)	1985 weekdays 12-1 p.m.		CMB/trajectory	3	9	MV 61% of 9 VOC species sum	no comparison to EI
Wintertime Source-Reconciliation of Ambient Organics								
Aronian et al., Univ. Ill., 1989	Chicago (3 sites)	winter 8 am - noon	EPA	CMB	8	23	MV exh 35% of NMOC; gas vapor 5%; refineries 11%	good agreement with EI except refineries higher than EI
Source Reconciliation of Ambient Volatile Organic Compounds Measured in the 1990 Atlanta Summer Study: The Mobile Source Component								
Lewis and Conner, EPA AREAL, 1992	Atlanta (1 site)	1990 30-min diurnal	EPA	CMB	1	10	MV exh 40-100% of NMOC	source profile from local tunnel study
Toxic Volatile Organic Compounds in Urban Air in Illinois								
Sweet and Vermette, Ill. St. Water Surv., 1992	Chicago, E. St. Louis	1986-1990 various seasons	Ill. DENR	factor analysis/ CMB	6	12	MV accounts for most toxics on average day, less on polluted day	no NMOC analysis
Receptor Modeling of VOCs in Atlanta Georgia								
Kenski, Wadden, and Scheff, Univ. Ill., Lonneman, EPA, 1992	Atlanta (2 sites)	1984-86 summer 6-9 a.m.	EPA	CMB	4	29	MV exh 53% of NMOC; gas vapor 16%	MV exh lower than EI

APPENDIX A. VOC source apportionment/receptor modeling studies - continued.

No. / Study Name								
Researchers, Affiliation, Date	Location	Time	Sponsor	Approach	No. of profiles	No. of fitting species	Conclusions	Comments
Respeciation of Organic Gas Emissions and the Detection of Excess Unburned Gasoline in the Atmosphere								
Harley et al., Caltech, 1992	Los Angeles (9 sites)	1986, 1987 summer 4-hr avg and diurnal	EPRI	CMB	6	15	MV exhaust 35% of NMOC; unburnt gas major factor missing from EI	restricted fitting species to non-reactive VOC
Receptor Modeling of SCAQS Volatile Organic Compounds								
Gertler et al., DRI, 1993	Los Angeles (2 sites)	1987 SCAQS hourly	SCAQS	CMB	4	15-17	MV exh 60-70%	evap and refinery source could not be resolved
A Receptor Modeling Approach to VOC Emission Inventory Evaluation								
Kenski et al., Univ. Ill., 1993	Detroit Chicago Beaumont Atlanta Washington	1984-88 summer 6-9 a.m. and diurnal	EPA	CMB	7	29	MV exh: 14% BMT; 28% Det; 41% Chi; 53% Atl; 56% Wash	agreement with EI generally good
Receptor Modeling of Volatile Hydrocarbons Measured in the 1990 Atlanta Ozone Precursor Study								
Lewis et al., EPA, 1993	Atlanta (1 site)	1990 30-min diurnal	EPA	CMB, source profiles from GRACE/SAFER	8	36	Total MV 63-80%, depending on def. of NMOC	
Receptor Modeling of Volatile Organic Compound. 1. Emission Inventory and Validation								
Scheff and Wadden, Univ. Ill., 1993	Chicago (3 sites)	1987 summer 8-12	EPA, NSF	CMB, trajectory	8	23	MV 21% of 23-species sum; refinery 7%; gas vapor 7%	59% unidentified; MV good agreement with EI

APPENDIX A. VOC source apportionment/receptor modeling studies - continued.

No. / Study Name								
Researchers, Affiliation, Date	**Location**	**Time**	**Sponsor**	**Approach**	**No. of profiles**	**No. of fitting species**	**Conclusions**	**Comments**
Source Attribution of Toxic and Other VOC's in Columbus, Ohio								
Mukund et al., Battelle, 1994	Columbus (6 sites)	1989 summer 6-9 a.m.	EPA	CMB	5	16	MV exh 34% of 16-species sum; gas vapor 19%	primary focus on toxics
Validation of the Chemical Mass Balance Receptor Model Applied to Hydrocarbon Source Apportionment in the Souther California Air Quality Study								
Fujita, Watson, Chow, Lu. 1994.	CA South Coast Air Basin (9 sites)	1987 fall		CMB	23			
Comparison of Atlanta Emission Inventory with Ambient Data Using Chemical Mass Balance Receptor Modeling								
Conner, Collins, Lonneman, Seila EPA, 1994	Atlanta (6 sites)	1990 summer	EPA	CMB	3	18	EI undrestimates mobile sources; EI overestimates combined area & point	Ambient-derived source estimates expressed as ranges.
Volatile Organic Compound Source Apportionment for the Coastal Oxidant Assessment for southeast Texas Study (Draft)								
Lee, Fjuita	Houston (2 sites)	August 1993	TNRCC	CMB				

APPENDIX B. VOC source profile studies.

No. / Study Name							
Researchers, Affiliation, Date	**Objectives**	**Location**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
Source Fingerprints for Receptor Modeling of Volatile Organics							
Scheff et al., Ill. Inst. of Tech., 1989	develop VOC source fingerprints for CMB		source profiles from literature	EPA, NSF	lit. review	10 source profiles developed	MV exhaust profile from Sigsby; gas vapor profile from winter blend
Volatile Organic Compound (VOC)/particulate Matter (PM) Speciation Data System, Version 1.4							
VOC/PM Speciation Data System, EPA, 1991	library of source profiles		VOC and PM source profiles	EPA	lit. review and eval.; some new data generated	over 700 profiles	MV profiles have been updated since 1991
Source Fingerprints for Volatile Non-Methane Hydrocarbons							
Doskey et al., Argonne, 1992	VOC source fingerprints	Chicago	source profiles generated	Ill. DENR	ambient VOC measurements in impacted areas	evap profiles are sensitive to season and grade of gasoline	used parking garage to obtain cold start and hot soak profiles
The Observation of a C5 Alcohol Emission in a North American Pine Forest							
Goldan et al., NOAA, 1993	characterize biogenic emissions	Niwot Ridge, Colorado	ambient VOC in remote forested area	NOAA	ambient meas.	new biogenic species, emissions = isoprene	large meas. uncertainty
Improvement of the Speciation Profiles Used in the Development of the 1991 LMOS Emission Inventory							
Korc and Chinkin, STI, 1993	review of VOC source profiles used in EI		VOC source profiles from EPA, CARB, and CIT	LADCO	lit review	replace EPA profiles for gas. evap. and surf. coating	used ambient data to identify possible problems with the profiles

APPENDIX B. VOC source profile studies. - continued.

No. / Study Name							
Researchers, Affiliation, Date	**Objectives**	**Location**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
Vehicle-Related Hydrocarbon Source Compositions from Ambient Data: The GRACE/SAFER Method							
Henry, USC, Lewis, EPA, and Conner, USC, 1994	development of VOC source profiles for CMB	Atlanta (1 site)	ambient NMOC	EPA	develop GRACE/SAFER method to extract source profiles from ambient data	develop city-specific profiles for "roadway", whole gasoline, and gasoline vapor	assumes acetylene is a tracer for MV exhaust

APPENDIX C. AMBIENT RATIO STUDIES.

Study Name								
Researchers, Affiliation, Date	**Objectives**	**Location**	**Time**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
A Review of NMOC, NOx, and NMOC/NOx Ratios Measured in 1984 and 1985								
Baugues, EPA, 1986	develop EKMA inputs, assess MV component	30 cities	1984-85 summer avg 6-9 a.m.	ambient NMOC and NO_x	EPA	acetylene as MV tracer; used NMOC:acetylene = 27 for MV	MV 18-88% of NMOC; lowest in Houston; higher than EI	EI not adjusted for time of day or species meas.
Speciated Hydrocarbon and NOx Comparisons at SCAQS and Receptor Sites								
Lonneman et al., EPA, 1989	develop EKMA inputs	Los Angeles, Long Beach, Claremont	1987 summer (5 days) 6-9, 12-3, and 3-6	ambient NMOC and NO_y (SCAQS)	EPA	ambient $NMOC:NO_y$ at source and receptor sites	$NMOC:NO_y$ lower at receptor site	no comparison to EI $NMOC:NO_x$
Reconciling Differences Between Ambient and Emission Inventory Derived NMOC/NOx Ratios: Implications for Emission Inventories								
Baugues, EPA, 1991	EI validation	16 cities	1985	ambient NMOC and NO_x	EPA	adjust EI to provide best comparison with ambient $NMOC:NO_x$	EI ratios average 23% lower than ambient	rule effectiveness assumptions have large effect
Comparison of Emission Inventory and Ambient Concentration Ratios of CO, NMOG, and NOx in California's South Coast Air Basin								
Fujita et al., CARB, 1992	EI validation	Los Angeles (8 sites)	1987 summer, fall avg. 7-8 a.m.	SCAQS ambient NMOC, CO, NO_x	CARB	comparison of ambient and EI $NMOC:NO_x$ and $CO:NO_x$ ratios	ambient ratios higher than EI; MV emis. underest.	speciated VOC data used qualitatively
Comparison of Emission Inventory and Ambient Concentration Ratios of NMOC, NOx, and CO in the Lake Michigan Air Quality Region								
Korc et al., STI, 1993	EI validation	Chicago, Gary, Milwaukee	1991 summer 7-9 a.m.	LMOS ambient NMOC, CO, NO_x	LADCO	ambient $NMOC:NO_x$ and $CO:NO_x$ ratios and VOC mass fractions	ambient ratios higher than EI; MV emis. underest.	speciated VOC compared to speciated EI

APPENDIX C. Ambient ratio studies - continued.

Study Name								
Researchers, Affiliation, Date	**Objectives**	**Location**	**Time**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
Use of PAMS Data to Evaluate the Texas Coast Emission Inventory								
Korc et al, STI, 1995	*EI validation*	*Southeast Texas*	*1993 summer 1-8 a.m.*	*COAST ambient NMOC, NO$_x$*	*EPA*	*comparison of ambient and EI NMHC:NO$_x$ ratios*		